NAWCWPNS TP 8364

Intrinsically Electrically Conducting Polymers as Corrosion Inhibiting Coatings

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APRIL 1998

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Naval Air Warfare Center Weapons Division

FOREWORD

The history of conducting polymer research is reviewed and recent results in the area of conducting polymers as corrosion protective coatings are presented and discussed in this report.

This report describes work supported by the Office of Naval Research, the Naval Air Warfare Center Weapons Division, and the Tomahawk/Cruise Missile Program and has been reviewed for technical accuracy by Geoffrey A. Lindsay.

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24 April 1998

Under authority of
RAND H. FISHER
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Commander

Released for publication by
S. HAALAND
Director for Research & Engineering

NAWCWPNS Technical Publication 8364

Published by .... Technical Information Division
Collation .... Cover, 9 leaves
First printing .... 27 copies

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*

2. REPORT DATE
April 1998

3. REPORT TYPE AND DATES COVERED
Review, Aug 95-Apr 97

4. TITLE AND SUBTITLE
Intrinsically Electrically Conducting Polymers as Corrosion Inhibiting Coatings (U)

5. FUNDING NUMBERS
PE: 28009N
Project: Tomahawk Cruise Missiles
Task: Corrosion Testing
Work Unit: PMA-280-96-06

6. AUTHORS
John D. Stenger-Smith, Peter Zarras, Melvin H. Miles, and John G. Nelson

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Naval Air Warfare Center Weapons Division
China Lake, CA 93555-6100

8. PERFORMING ORGANIZATION REPORT NUMBER
NAWCWPNS TP 8364

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
Tomahawk Cruise Missile Program Office
Patuxent River, MD 20670

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION /AVAILABILITY STATEMENT

A Statement; public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

(U) The history of conducting polymer research is reviewed and recent results in the area of conducting polymers as corrosion protective coatings are presented and discussed.

14. SUBJECT TERMS

Conducting polymer, Corrosion protection coatings, Synthesis

15. NUMBER OF PAGES
16

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	**UNCLASSIFIED**	**UNCLASSIFIED**	**UL**

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ACKNOWLEDGMENTS

The author would like to thank the Office of Naval Research, Naval Air Warfare Center Weapons Division, and the Tomahawk/Cruise Program for funding. Special thanks to Dr. John W. Fischer and Joseph Oliver for their encouragement.

HISTORY AND INTRODUCTION

This report is a history of research on conducting polymers and will present recent results in the area of conducting polymers as corrosion-protective coatings. On a historical note, polyaniline was first made as far back as 1862 by Letheby (Reference 1). Known as "aniline black" this material was formed by oxidation of aniline under mild conditions (References 2 and 3). Aniline black was an important material for dyeing and printing (Reference 4).

Conducting polymer research has roots back to the 1960s when Pohl, Katon, and others first synthesized and characterized semiconducting polymers (References 5 through 7) and conjugated polymers (Reference 8). The discovery of the high conductivity of poly(sulfurnitride) $(SN)_x$, a polymeric inorganic explosive (Reference 9), and its interesting electrical properties (References 10 through 16) was a step towards conducting polymers as they are known today.

The beginning of conducting polymer research began nearly a quarter of a century ago, when films of polyacetylene were found to exhibit profound increases in electrical conductivity when exposed to iodine vapor (References 17 and 18). This was the first report of polymers with high-electrical conductivity. The procedure for synthesizing polyacetylene was based upon a route discovered in 1974 by Shirikawa through serendipitous addition of a thousand times the normal amount of catalyst during the polymerization of acetylene (Reference 19).

Over the past two decades, there have been several excellent reviews on conducting polymers (References 20 through 34). Conducting polymer research is evolving rapidly enough that yearly reviews are almost a necessity. Today, there are hundreds of articles on conducting polymer research published every year. A journal entitled *Synthetic Metals* is almost exclusively dedicated to reporting on various aspects of conducting polymer research.

DEFINITIONS

The conducting forms are usually classified as the cation salts of highly conjugated polymers. The cation salts are obtained by electrochemical oxidation and electrochemical polymerization (Reference 35) or chemical oxidation (removal of an electron). It is also possible to obtain the anion salts of the same highly conjugated polymers, which are also conducting but much less stable than the cation counterparts, by either electrochemical reduction or by treatment with reagents such as solutions of sodium naphthalide (References 36 and 37).

In general, a conjugated backbone and/or a backbone that has a low enough oxidation potential is necessary but not sufficient for the electrically conducting form of a polymer to remain stable in the presence of air and water or end-use conditions such as inside an automobile or home.

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For clarity, the following definitions and abbreviations are given and will be referred to for the remainder of this review.

Oxidized (conducting) is the form of the polymer that has had electrons removed from the backbone, resulting in (radical) cations.

Neutral (insulating polymer) is the form of the polymer in its uncharged state. This can be referred to as a "reduced" form of the oxidized polymer. For the sake of clarity in this report, the phrase "neutral" or "insulating" will be used.

Reduced (conducting) is the form of the polymer that has had electrons added to the backbone resulting in (radical) anions. The difference between the oxidation potential and the reduction potential is roughly equal to the electronic band gap. It is not unusual that this form of conducting polymers has not been isolated since reduction potentials are usually less than -1.0 volts versus the saturated calomel electrode (SCE). It may be possible to isolate both forms of the polymer with some of the low bandgap materials being synthesized and as stronger electron acceptors are incorporated into conducting polymer backbones. Figure 1 shows some structures of conducting polymers.

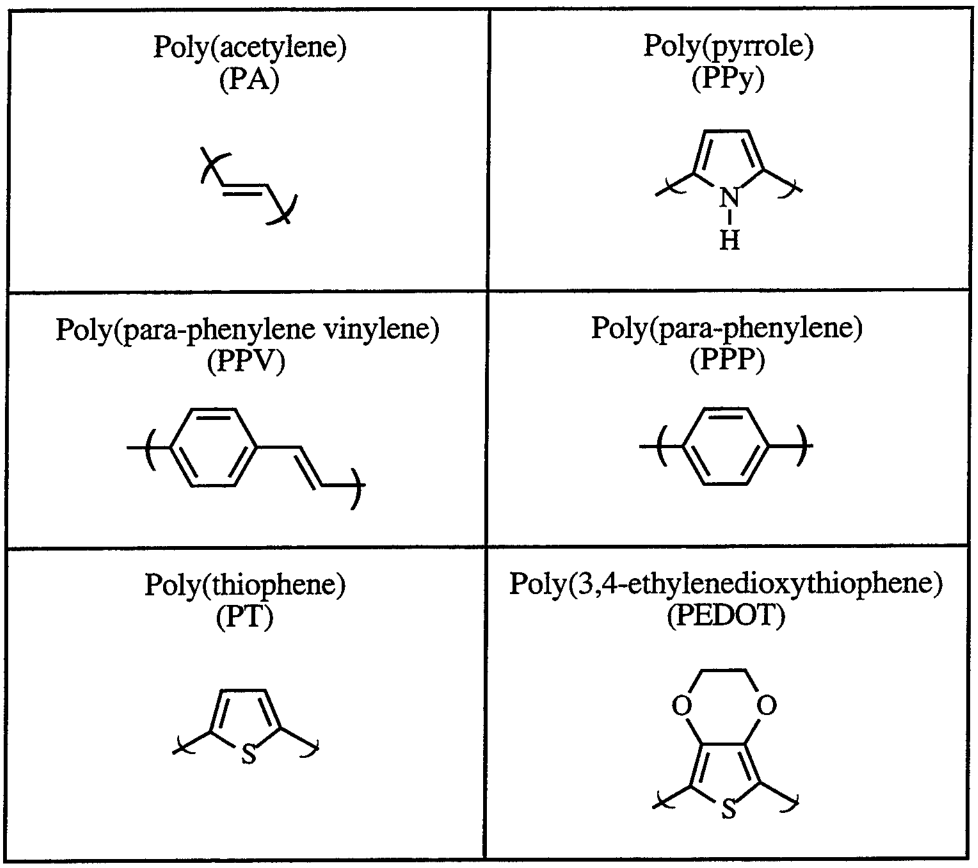
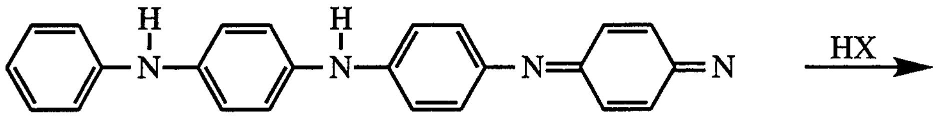
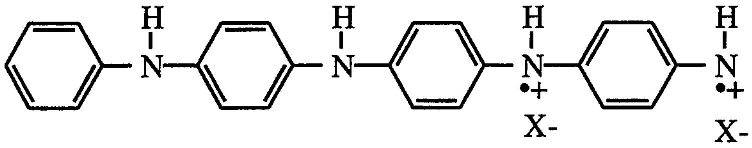


FIGURE 1. Structures of Conjugated Polymers in Their Respective Neutral Forms.

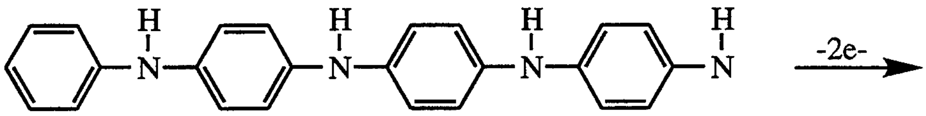
Polyaniline is usually obtained by protonation of what is called the emeraldine base form, shown in Figure 2.



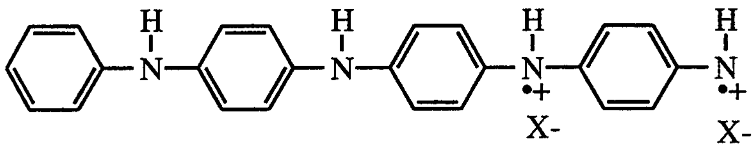
Emeraldine Base



Emeraldine Salt (Conducting)



Leucoemeraldine



Emeraldine Salt (Conducting)

FIGURE 2. Structures of Polyaniline.

The protonation reaction does not change the number of electrons in the polymer backbone. However, starting at the leucoemeraldine form of polyaniline, one would obtain the emeraldine salt (conducting) form of polyaniline by an oxidation reaction. Protonic doping has also been observed in the case of alkoxy substituted poly(para-phenylene vinylene) (PPV) (References 38 and 39).

CORROSION PROTECTION

In the area of potential applications, conducting polymers are used as replacements for metals because the conducting polymers have potentially unique and or superior properties, or because the metals are toxic or damage the environment.

Current methods of corrosion protection (particularly marine coatings) (Reference 40) do not last very long and are coming under increased scrutiny by the Environmental Protection Agency (EPA). For example, the use of chromium and cadmium for anti-corrosion coatings will soon be banned. A mechanism for corrosion protection involves

the use of a sacrificial electrode, such as a zinc coating, which will corrode (oxidize) in the place of the substrate. However, the coatings do not last very long. The oxidized zinc metal is dissolved by water or moisture. For this reason there are extreme environmental concerns since toxic metals are being released. Barrier coatings such as epoxy are employed extensively but are not very durable/robust once a pit or hole in the coating has been formed. The corrosive species then attacks the underlying metal and, thereby, increases the exposed surface, accelerating the corrosion process.

The corrosion inhibiting properties of conducting polymers were suggested by MacDiarmid in 1985. Initial studies on the protection of metal surfaces against corrosion by conducting polymers was reported in the literature that same year (Reference 41). Much of the work on corrosion protection has focused on polyaniline (PANI) (References 42 through 46), but also has been extended to other conjugated polymers (References 47 through 50). A major type of corrosion occurs by oxidation of a metallic surface by a saltwater medium to produce oxides and hydroxides. As these form, soluble species are produced, the surface pits increase the surface area, and the rate of decomposition accelerates. One way to provide corrosion protection is to coat the metal with a barrier to prevent the reactive species from reaching the surface. Galvanization with zinc (or other metal with low enough oxidation potential) prevents corrosion via the creation of an interfacial potential at the metal:zinc interface. The zinc will corrode preferentially. While the reactive species may come in contact with the metal, the increased oxidation potential causes the metal to be unreactive. Corrosion is inhibited.

Prior work utilizing PANI as a corrosion-protection coating shows that it works quite well. In fact, exposed metal surfaces adjacent to conducting polymer coatings (scratches or edges) are unreactive to corrosion as reported by Thompson and co-workers (References 51 and 52). The corrosion protection properties of PANI on aluminum have also been studied (Reference 53).

At present, some conducting polymers (in their neutral, non-conducting states) are soluble in organic solvents. Various types of surfactant counter-ions have been used with PANI to make the conducting form of polyaniline soluble in organic solvents.

There is a huge commercial potential for the use of conducting polymers as corrosion inhibiting coatings. Some estimates indicate that corrosion costs United States industry tens of billions of dollars per year (Reference 54).

There are several proposed mechanisms for corrosion protection, one or more of which could be occurring at any time. The first is a simple galvanic process by which the polymer has a lower oxidation potential than the metal it is protecting; the polymer is preferentially oxidized. Because oxidized polymers are usually insoluble and, therefore, do not dissolve away as zinc does, corrosion protection with conducting polymers should last longer.

Another proposed mechanism is that the polymer reacts with the surface of the metal, requiring that the polymer have an oxidation potential higher than that of the metal. The surface of the metal reacts with the polymer and forms a passivating layer (Reference 55) which inhibits further corrosion by either setting up a barrier or by changing the surface potential or both.

One possible disadvantage to using polyaniline is that the corrosion-protection ability is pH dependent. In acidic media, polyaniline-coated mild steel coupons corrode a hundred times slower than counterparts, while in pH 7 media, the PANI-coated material corrodes twice as slowly (References 56 and 57). Because the pH of seawater is around 8.0 to 9.4 depending upon season and location, it is unclear or unproven that PANI will provide any additional corrosion protection for ocean-going vessels. This could be explained by the pH dependence of the structure of PANI. At low pH, the conducting emeraldine salt is the predominant form; at high pH, the non-conducting emeraldine base is the predominant form. It appears that the conducting form is required for the formation of the passivation layer. In summary, the amount of corrosion protection is controlled by the type of polyaniline (emeraldine base versus emeraldine salt) and the characteristics of the corrosion environment (acidic medium, aqueous sodium chloride, or seawater) and also by adhesion to the substrate. Studies on the marine application of corrosion protection capability of conducting polymers will need to be performed in solutions isotonic with seawater and/or a salt fog according to American Society for Testing of Materials (ASTM) methods (References 58). For corrosion protection, it may be necessary to develop conducting polymers that do not have the pH dependence of conductivity that PANI has.

SYNTHESIS OF POLY(2,5-BIS(N-METHYL-N-PROPYL)AMINO PHENYLENE VINYLENE) (BAMPPV)

The addition of bis(dialkyl amino) substituents onto the PPV backbone is of interest for several reasons. First, the amino groups are generally stronger electron donors than alkoxy groups (provided that the resulting amino substituted polymer structure is planar) and should bring the oxidation potential of the polymer down around 0 volts vs. SCE, making the conducting polymer even more stable. Also, amine functionalized polymer should adhere fairly well to aluminum. Finally, amino groups can also be quarternized, which could be exploited to make the polymer water soluble.

The synthesis of amino functional PPV presented some serious synthetic challenges (Reference 59). Usually, a radical halogenated step is used in making the precursors to PPV. For example, 1,4-dimethyl benzene would be chlorinated or brominated to make a precursor to PPV. Although this method can be adapted well for the alkoxy derivatives, it cannot be used for amino derivatives because the reaction is dangerously exothermic. The danger of this type of reaction was established back in 1957, when a fatal accident occurred (Reference 60). Another method, used generally for dialkoxy derivatives, is to chloromethylate the dialkoxy substituted compounds. This reaction will not work with amines because the acidic conditions used will protonate the amine making it unreactive.

Therefore, another synthetic strategy was developed. This method, shown in Figure 3, does not involve any of the problem steps mentioned above.

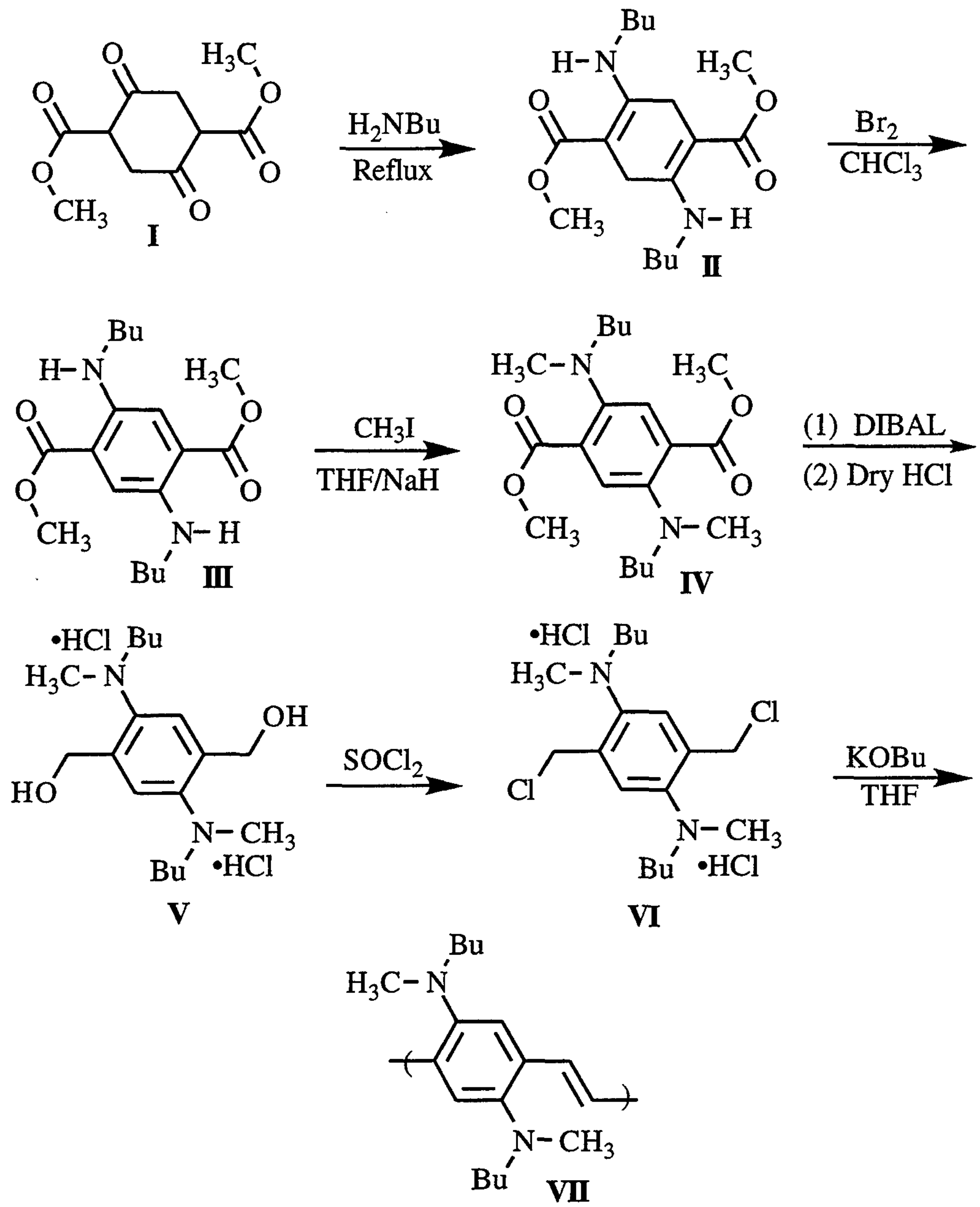


FIGURE 3. Synthesis of Bis(dialkylamino) PPV.

This method allows the synthesis of fairly pure polymer (Reference 61) and is being improved to allow for scaleup. The electrical and electrochemical properties of this polymer are currently being studied. The neutral form of the polymer is orange-red in color and the absorption maximum is 460 nanometers. This absorption maximum is much higher in energy than expected, so it is possible that the polymer backbone is non-planar.

CORROSION STUDIES OF BAMPPV

BAMPPV was coated onto Type II anodized aluminum T3 plates (5.1 x 5.1 x 0.15 cm, A = 55 cm^2) in saltwater for one month of alternate immersion in seawater and exposure to air. Constant current (galvanostatic and constant potential (potentiostatic) methods were used to investigate the corrosion of these aluminum plates. The electrochemical studies were conducted in concentrated saltwater solutions by dissolving 70.13 grams of sea salt (Bio-Sea Marine Mix) in 1200 milliliters of de-ionized water. This produced a solution of approximately 1 molar in NaCl with a specific gravity of 1.04257, with a pH of approximately 8, which contained trace elements of seawater.

Potentiostatic and galvanostatic studies of an (unanodized) aluminum plate in this salt solution are shown in Figure 4. The two methods give approximately the same results, showing the pitting potential (the potential at which the current increases rapidly due to corrosion) near -0.6 volt vs. Ag/AgCl.

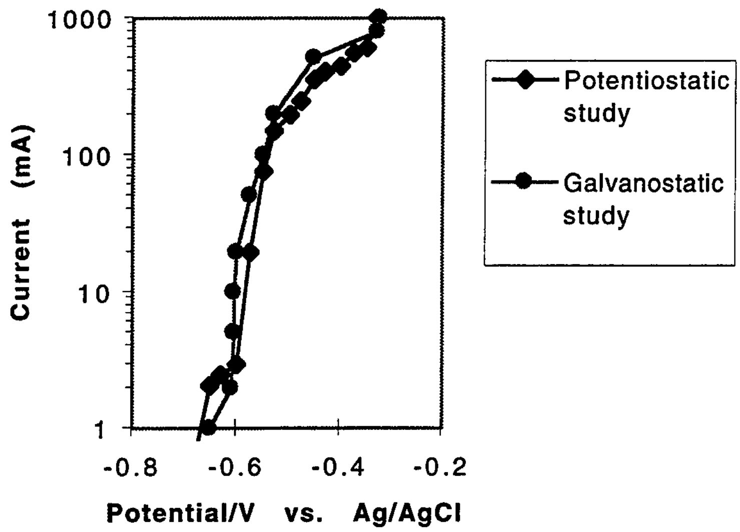


FIGURE 4. Potentiostatic and Galvanostatic Electrochemical Studies of an Unanodized-Aluminum Plate in the Sea Salt Solution. The squares are the potentiostatic study.

The electrochemical behavior is very different for anodized-aluminum plates, as shown in Figure 5. There is no measurable current for this potentiostatic study to within 0.001 milliampere from -0.600 to -0.300 volts. The pitting potential is shifted markedly from that shown in Figure 4 to about -0.28 volts vs. Ag/AgCl. Despite the anodic potentials applied in Figure 5, currents larger than 15 milliamperes are not observed. Further increases in potentials out to 3.00 volts were investigated; the largest current obtained was only 25 milliamperes. Detailed examination of the aluminum plate indicated that a few isolated regions on the edges of the plate were the main contributors to the anodic current. During the time period of this potentiostatic study, the anodic current gave a yield of 1.380 coulombs. Also shown in Figure 5 are exactly the same potentiostatic measurements for an anodized aluminum plate coated with BAMPPV. The striking feature is that very little corrosion current is observed. There is no measurable current to within

0.001 milliampere from -0.600 to +0.45 volts. The corrosion potential, if there is one, is near 0.525 volts vs. Ag/AgCl. This increase in overvoltage corresponds to an activation energy barrier increase of 57.9 kilojoules/mole. The current increases only slightly to 0.071 milliampere at 0.80 volts and then decreases. There is no further increase in the current even out to 3.00 volts. The coulombic measurements during this potentiostatic study yielded only 0.00358 coulombs. Therefore, based upon the coulombic measurements, the polymer-coated anodized-aluminum plate yielded only 0.26% of the corrosion measured for the uncoated anodized-aluminum plate. This is quantitative evidence that polymer coatings can substantially reduce pitting corrosion of aluminum. In addition to the studies shown in Figures 4 and 5, several long-term (days) constant-current electrolysis experiments were conducted with polymer-coated and uncoated-aluminum plates. In each long-term study, the corrosion pits that developed were always significantly less for the polymer-coated plates. Figure 5 shows a potentiostatic study after the plates were alternately immersed and exposed to air for an additional 5 months. The pitting potential is still much higher for the coated film (0.225 volts vs. Ag/AgCl), which is about 75% of the initial value, giving an activation energy barrier for corrosion of 43.4 kilojoules/mole.

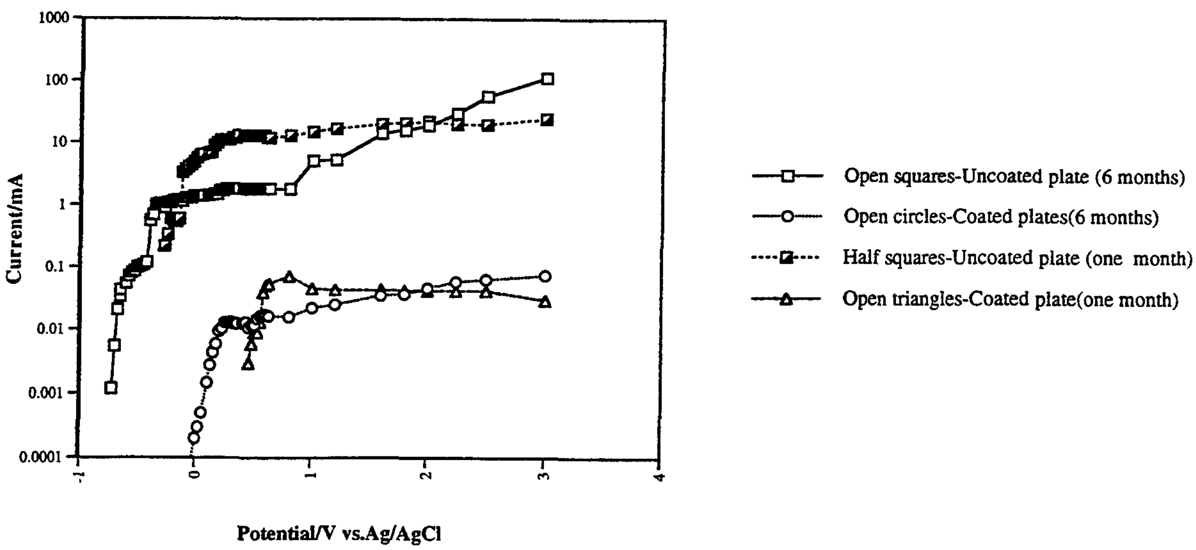
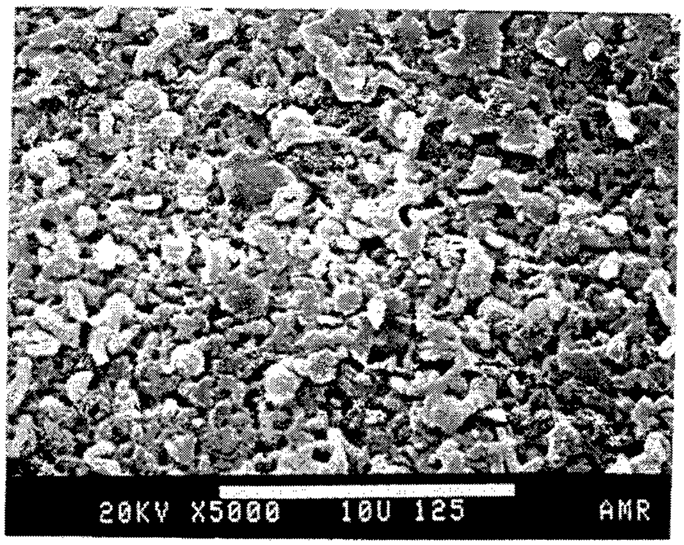


FIGURE 5. Potentiostatic Electrochemical Studies of Anodized-Aluminum Plates.

Scanning electron microscopy (SEM) was also performed on unanodized bare-aluminum plates and BAMPPV-coated unanodized-aluminum plates. The results from the SEM, shown in Figure 6, show that the polymer coating provides a significant degree of corrosion protection.

(a)



(b)

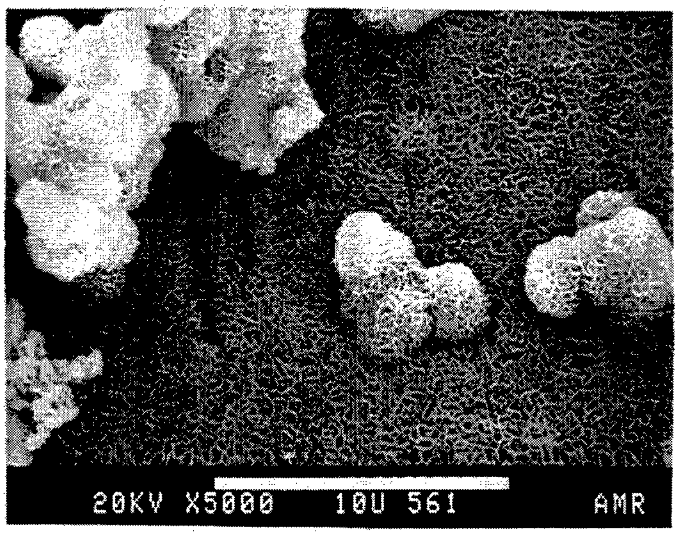


FIGURE 6. (a) PPV-Coated Aluminum with Minimal Corrosion and (b) Uncoated Aluminum with Severe Corrosion.

SUMMARY

A new conducting polymer, poly(2,5-bis(n-methyl-n-propyl)amino phenylene vinylene), was synthesized and characterized. Investigators have demonstrated that this conducting polymer is a very promising candidate for corrosion protection of aluminum plates.

Future work will involve the comparison of the corrosion resistance of a chrome-conversion coated-aluminum plate to a polymer-coated untreated-aluminum plate.

THE FUTURE OF CONDUCTING POLYMERS

New and exciting applications for conducting polymers occur almost biennially, so there is no lack of possibilities. Conducting polymer research is, however, at a critical juncture between laboratory curiosity and commercial viability. Although conducting polymer research will not fade away entirely, the amount of financial support will depend upon evolutionary development and commercialization.

An area where conducting polymers has great potential is in corrosion protection. If superior performance of conducting polymers can be demonstrated under Fleet conditions (which vary greatly depending upon use and environment), there is a potential billion dollar savings to the Navy.

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